

## WO0004775

Publication Title:

MOLLUSCICIDAL COMPOSITION

Abstract:

Abstract of WO0004775

The composition comprises at least one molluscicide for target molluscs, and at least one deterrent for non-target invertebrates, wherein the deterrent is incorporated in the composition so as to have substantially no effect on target molluscs feeding on the composition and to substantially preclude feeding on the composition by the non-target organisms. Examples of possible deterrents include bicyclic compounds, monohydric or polyhydric C6-10 alcohol, and a substituted 6-membered carbocyclic ring. Data supplied from the esp@cenet database - Worldwide c60

-----  
Courtesy of <http://v3.espacenet.com>

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 7 :</b> A01N 47/22, 47/24, 25/00 // (A01N 47/22, 65:00, 61:00, 49:00, 43:90, 37:18, 37:10, 35:06, 35:02, 31:08, 31:06, 35:02, 31:08, 31:06, 31:02, 27:00, 25:00) (A01N 47/24, 65:00, 61:00, 49:00, 43:90, 37:18, 37:10, 35:06, 35:02, 31:08, 31:06, 31:02, 27 :00, 25 :00)	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/04775</b>
		<b>(43) International Publication Date:</b> 3 February 2000 (03.02.00)
<b>(21) International Application Number:</b> PCT/GB99/02394	<b>(74) Agent:</b> AUSTIN, Hedley, William; Urquhart-Dykes & Lord, Alexandra House, Alexandra Road, Swansea SA1 5ED (GB).	
<b>(22) International Filing Date:</b> 23 July 1999 (23.07.99)		
<b>(30) Priority Data:</b> 9816039.3 23 July 1998 (23.07.98) GB		
<b>(71) Applicants (for all designated States except US):</b> UNIVERSITY COLLEGE CARDIFF CONSULTANTS LIMITED [GB/GB]; 55 Park Place, P.O. Box 923, Cardiff CF10 3AT (GB). INSECT INVESTIGATIONS LIMITED [GB/GB]; School of Pure & Applied Biology, University of Wales, P.O. Box 915, Cardiff CF1 3TL (GB).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
<b>(72) Inventor; and</b>		
<b>(75) Inventor/Applicant (for US only):</b> SYMONSON, William, Oliver, Christian [GB/GB]; Gallt Hyfryd, Pontfadog, Llangollen, Clwyd LL20 7AG (GB).		
<b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>		
<b>(54) Title:</b> MOLLUSCICIDAL COMPOSITION		
<b>(57) Abstract</b>		
<p>The composition comprises at least one molluscicide for target molluscs, and at least one deterrent for non-target invertebrates, wherein the deterrent is incorporated in the composition so as to have substantially no effect on target molluscs feeding on the composition and to substantially preclude feeding on the composition by the non-target organisms. Examples of possible deterrents include bicyclic compounds, monohydric or polyhydric C<sub>6-10</sub> alcohol, and a substituted 6-membered carbocyclic ring.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

### Molluscicidal Composition

The present invention is concerned with a molluscicidal composition, a process of preparing the composition and the use thereof.

Slugs and snails are major pests in arable crops; particularly the field slug *Deroceras reticulatum*, with its ability to hollow grain and destroy newly emerged shoots and leaves. Current control measures rely primarily on the use of baited pellets containing a molluscicide, such as methiocarb. Although such pellets have been effective due to the toxicity of molluscicides, such as methiocarb, the latter has also been implicated in the poisoning of non-target organisms. This has been particularly problematic where the non-target organisms are themselves involved in pest control. For example, non-target insects, such as carabid beetles, which are known to be important natural control agents for several crop pests (including slugs), have been known to have died following ingestion of such methiocarb-containing pellets.

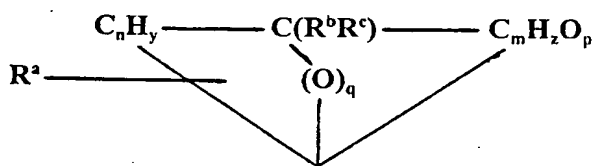
There does, therefore, exist a need for improved, more specific molluscicidal compositions palatable only to molluscs, and the present invention provides such improved compositions, processes of preparation and uses thereof.

According to the present invention there is provided a molluscicidal composition comprising at least one molluscicide for target molluscs, and at least one deterrent for non-target invertebrates, wherein the deterrent is incorporated in the composition so as to have substantially no effect on target molluscs feeding on the composition and to substantially preclude feeding on the composition by the non-target organisms.

The term "molluscicide" as used herein denotes an agent for destroying molluscs, and typically a composition according to the present invention is employed in destroying slugs, such as slugs of the species *Deroceras reticulatum*. Suitable molluscicides for use in the present invention include methiocarb or thiodicarb, although other available molluscicides can be used. Preferably, methiocarb is employed as a molluscicide in the present invention.

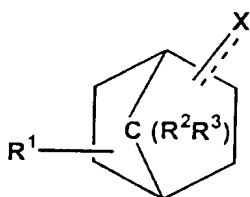
The term "deterrent" as used herein typically denotes a substance that can elicit avoidance behaviour in the non-target invertebrates, through detection of volatile or non-volatile chemicals via receptors on antennae, palps or other mouthparts of the non-target invertebrates. The deterrent employed in the present invention is selected so as to have substantially no effect on feeding molluscs, in other words mollusc feeding is substantially uninhibited by the inclusion of the deterrent in the composition. In this way, the present invention provides a molluscicidal composition that is unpalatable to the non-target invertebrates, but palatable to the target molluscs, and as such is substantially specific for the target molluscs. The non-target invertebrates are preferably insects (such as carabids).

According to a first aspect of the present invention, the deterrent comprises a bicyclic compound. Suitable bicyclic compounds can be represented by general formula (I)

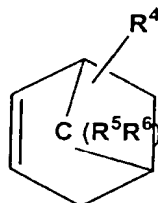


where n is 2 to 4, y is 2n or 2n-2, m is 0 to 3, z is 2m if p is 0 or 1, or z is m if p is 1, and q is 0 or 1; R<sup>a</sup>, R<sup>b</sup> and R<sup>c</sup> each independently represent hydrogen or C<sub>1-4</sub> alkyl. The oxygen in the C<sub>m</sub>H<sub>z</sub>O<sub>p</sub> group may be in a carbonyl group or a hydroxyl group, with appropriate values for m and z.

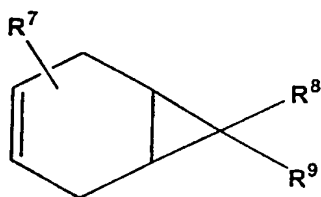
Preferred bicyclic compounds for use as a deterrent can be represented by any of formulae (II), (III), (IV) or (V)



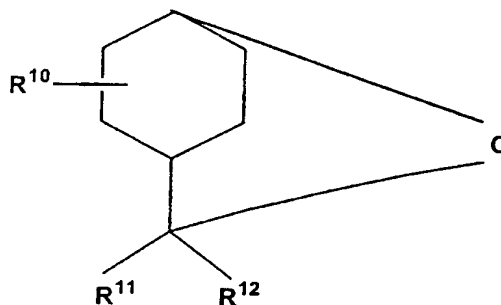
(II)



(III)



(IV)

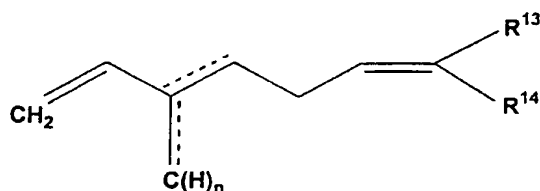


(V)

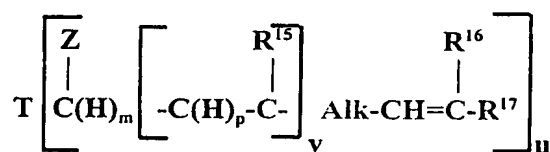
where  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$  and  $R^{12}$  each independently represent hydrogen or  $C_{1-4}$  alkyl, X represents oxygen or hydroxy and ----- represents a bond in the case where X represents oxygen.

Preferred compounds for use as a deterrent according to the first aspect of the present invention include camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one), borneol (*endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol), eucalyptol (1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane),  $\alpha$ -pinene (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene), D-3-carene (3,7,7-trimethylbicyclo[4.1.0]hept-3-ene) or the like.

According to a second aspect of the present invention, the deterrent comprises a monohydric or polyhydric C<sub>6-10</sub> alcohol or a compound of formula (VI) or (VII)



(VI)



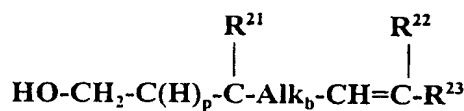
(VII)

where R<sup>13</sup>, R<sup>14</sup>, R<sup>15</sup>, R<sup>16</sup>, and R<sup>17</sup>, each independently represent C<sub>1-3</sub> alkyl, T is hydrogen or an aliphatic hydrocarbon group, Alk is a C<sub>1-3</sub> alkylene chain, Z is oxygen or hydroxy, n is 2 or 3, m is 0 or 1, v is 1 when T is hydrogen or 0 in all other cases, u is 1 or 2, p is 1 or 2 and ----- represents the optional presence of a bond.

Preferred compounds of formula (VII) for use as a deterrent can be represented by formulae (VIII) and (IX)



(VIII)



(IX)

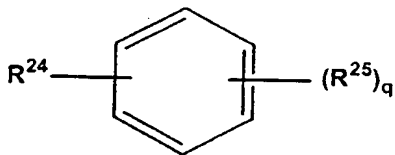
where R<sup>18</sup>, R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup>, R<sup>22</sup>, and R<sup>23</sup> each independently represent C<sub>1-3</sub> alkyl, Alk<sub>a</sub> and Alk<sub>b</sub> independently represent a C<sub>1-3</sub> alkylene chain, Z is oxygen or hydroxy, m is 0 or 1, and p is 1 or 2.

Preferred deterrents for use according to the second aspect of the present invention include one or more of 2-ethylhexane-1,3-diol, citronellol (3,7-dimethyl-6-octen-1-ol), octan-1-ol,  $\beta$ -myrcene (7-methyl-3-methylene-octa-1,6-diene), nerol (*cis*-3,7-dimethyl-octa-2,6-dien-1-ol),  $\beta$ -ocimene (3,7-dimethyl-octa-1,3,6-triene), sulcatol (6-methyl-5-hepten-2-ol), sulcatone (6-methyl-5-hepten-2-one) and lycopene or a material containing lycopene. More particularly, sulcatol, sulcatone and lycopene are especially preferred deterrents for use according to the second aspect of the present invention.

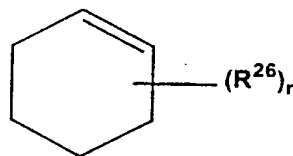
Lycopene is a precursor of sulcatone and is typically found in tomato skins. Lycopene may be advantageous in that only small amounts are lost during heat treatment, for example, 20% loss of lycopene when it is heated to 65 - 100 °C for 3 hours. Heat treatment may be used during production of molluscicidal compositions according to the invention, particularly when the latter are in the form of pellets.

According to a third aspect of the present invention, the deterrent comprises a substituted 6-membered carbocyclic ring, where the ring is either benzene or cyclohexene, and where the substituents are one or more of  $C_{1-4}$  alkyl,  $C_{2-4}$  alkenyl,  $C_{1-4}$  alkoxy, hydroxy,  $CO_2C_{1-4}$  alkyl,  $CON(C_{1-4} \text{ alkyl})_2$  and  $C_{1-4}$  alkylene $CON(C_{1-4} \text{ alkyl})_2$ .

Suitably, the third aspect of the present invention employs deterrents of formulae (X) or (XI)



(X)



(XI)

where  $R^{24}$  represents hydrogen,  $C_{1-4}$  alkyl or  $C_{2-4}$  alkenyl,  $R^{25}$  represents  $C_{1-4}$  alkyl,  $C_{1-4}$  alkoxy, hydroxy,  $CO_2C_{1-4}$  alkyl,  $CON(C_{1-4} \text{ alkyl})_2$  or  $C_{1-4}$  alkylene $CON(C_{1-4} \text{ alkyl})_2$ ,  $R^{26}$  represents  $C_{1-4}$  alkyl or  $C_{2-4}$  alkenyl,  $q$  is 1 or 2, and  $r$  is 1 or 2.

Preferred deterrents employed according to the third aspect of the present invention are one or more of eugenol (4-allyl-2-methoxyphenol), limonene (4-isopropyl-1-methyl-cyclohex-1-ene), *DEET* (*N,N*-diethyl-*m*-toluidine), *DEPA* (*N,N*-diethyl-phenyl-acetamide), *DMP* (dimethylphthalate) and thymol (5-methyl-2-isopropylphenol).

The above described deterrents are generally olfactive, volatile compounds. However, according to a fourth aspect of the present invention a non-volatile deterrent may be used in a composition according to the present invention. Suitably, a non-volatile deterrent for use in the present invention comprises a tetranortriterpenoid, such as azadirachtin or the like. A non-volatile deterrent of this type may be advantageous in facilitating preparation of a composition according to the present invention, for example facilitating incorporation into a molluscicidal pellet or the like.

Preferably, a deterrent employed in the present invention is one or more of a monohydric C<sub>6-10</sub> alcohol or a compound of formula (I), (III), (IV) or (VI). Preferred deterrents for use in the present invention include any of eucalyptol (1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane), octan-1-ol, borneol (*endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol), camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one), sulcatol (6-methyl-5-hepten-2-ol), sulcatone (6-methyl-5-hepten-2-one), and D-3-carene (3,7,7-trimethylbicyclo[4.1.0]hept-3-ene).

The most preferred deterrents for use in the present invention include any of borneol (*endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol), camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one), sulcatol (6-methyl-5-hepten-2-ol), sulcatone (6-methyl-5-hepten-2-one), and D-3-carene (3,7,7-trimethylbicyclo[4.1.0]hept-3-ene).

A deterrent employed in the present invention is suitably employed against invertebrates which are themselves important natural control agents for a number of crop pests, including molluscs. In particular, these non-target invertebrates can include insects, such as beetles, especially carabid beetles or the like.

Further ingredients which may be present include proteins, carbohydrates or the like, or surfactants, binders or the like. Such further ingredients may be bait materials (such as, for example, a yeast extract), which are attractive to slugs, or materials which act as foods for slugs.

Generally, a composition according to the present invention further comprises at least one inert carrier. The term "inert carrier" as used herein refers to a carrier suitable for use in molluscicidal compositions, which does not substantially adversely interact with the deterrent or molluscicide, or any other ingredients. The "inert carrier" may have a positive effect in that it may itself be attractive to slugs. An example of such a carrier is a starch, which is also a food for slugs.

Typically, inert carriers suitable for use in compositions according to the present invention comprise materials that can be intimately mixed with the deterrent and molluscicide suitable for use according to the present invention, together with any other optional ingredients which may be present. Intimate mixtures of the molluscicide, deterrent and one or more inert carrier, can suitably be shaped into conventional forms, such as pellets, blocks, pads or tapes, for use in accordance with the present invention. When pellets are used in accordance with the present invention, they are generally of a size of the order of substantially 2 by 5 mm.

There is further provided by the present invention a pellet comprising a molluscicidal composition substantially as herein before described, and optimally further comprising one or more inert carriers for the deterrent and molluscicide.

According to the present invention there is further provided use of a molluscicidal composition substantially as herein before described in destroying molluscs, and in particular destroying slugs, such as slugs of the species *Deroceras reticulatum*.

The present invention further provides use of a molluscicide in destroying molluscs, wherein the molluscicide is used in combination with at least one deterrent for non-target invertebrates. This use according to the present invention is suitably employed in destroying slugs substantially as described above.

The present invention further provides a method of destroying molluscs, which method comprises providing molluscs with a molluscicidal composition substantially as herein before described, and allowing the molluscs to ingest the molluscicidal composition.

There is also provided by the present invention a method of treating an environment with a molluscicidal composition substantially as herein before described, so as to effect substantial eradication of molluscs from the environment. Typically, the environment treated by a composition according to the present invention (referred to below as a treatment environment) is an arable area or pasture, a glasshouse, an area of ornamental plants or forestry seedlings or the like. Alternatively a composition according to the present invention may be employed in treating domestic or public gardens so as to substantially eradicate molluscs therefrom.

There is further provided by the present invention a method of deterring non-target invertebrates (and in particular the carabid beetle), from ingesting a molluscicide which has been employed in a treatment environment as described above, which method comprises treating the environment with a molluscicidal composition substantially as hereinbefore described, whereby the deterrent is present in sufficient quantity to substantially preclude ingestion of the molluscicide by the non-target invertebrates.

According to the present invention there is further provided a process of preparing a molluscicidal composition, which process comprises mixing at least one molluscicide for target molluscs and at least one deterrent for non-target invertebrates, so that deterrent incorporated in the composition has substantially no effect on target molluscs feeding on the composition and substantially precludes feeding on the composition by the non-target invertebrates.

Suitably a process according to the present invention optimally further comprises mixing the deterrent and molluscicide with one or more inert carriers therefor. Appropriately a process according to the present invention further comprises shaping the deterrent and molluscicide, and optimally the inert carrier, into a pellet, suitable for ingestion by molluscs.

The present invention further provides use of a molluscicide in the manufacture of a molluscicidal composition substantially as herein before described. The use comprises mixing the molluscicide with at least one deterrent for non-target invertebrates, and optionally one or more inert carriers therefor.

There is also provided use of at least one deterrent for non-target invertebrates in the manufacture of a molluscicidal composition substantially as herein before described. The use comprises mixing the deterrent with a molluscicide, and optimally further mixing with one or more inert carriers therefor.

According to yet a further aspect of the invention there is provided, in combination (for use in destroying molluscs):

at least one molluscicide for target molluscs; and

at least one deterrent for non-target invertebrates, whereby feeding target molluscs are substantially unaffected by the deterrent and non-target invertebrates are substantially precluded from feeding on the molluscicide by the deterrent.

The present invention will now be further illustrated by the following Example, which does not limit the scope of the invention in any way.

### Example

#### Electrophysiological screening

##### Electroantennogram

The electroantennogram (EAG) equipment employed is illustrated in Figure 1, where (1) represents a microscope, (2) represents a stimulus pipette, (3) represents an applicator, (4) represents a stimulus controller, (5) represents an operating computer, (6) represents a start pedal, (7) represents an antennal preparation, (8) represents a manipulator and (9) represents an amplifier.

A carabid, partially anaesthetised through chilling, was placed under a microscope (1) and a single antenna removed by cutting at the base where it enters the head. An electrode was then inserted into the base of the antenna before being earthed, this serving as the "indifferent" or "reference" electrode.

The extreme tip of the antenna was removed before several sensillary hairs were positioned into the tip of the "recording" electrode using "leitz" micromanipulator (8). The recording glass electrode had previously been trimmed to be a tight fit over the tip of the antenna to prevent Ringer solution from leaking out over the preparation, causing background instability and interference. Both electrodes consisted of Ag/AgCl wire contained in glass microelectrodes and partially filled with Rhodnius Ringer solution.

A continuous stream of purified air was passed over the preparation at a rate of 1L/min. This was both generated and maintained by stimulus controller (4). Test chemicals were then introduced into this air stream for a 0.5 second period and subsequently delivered to the preparation. This was achieved by blowing air over a strip of paper, on which 10  $\mu$ L of test chemical had previously been dosed. The filter paper was contained within stimulus pipette (2) which was then positioned into the centre of the air stream and test chemicals blown over antennal preparation (7). Before the chemicals were applied to preparation (7), hexane solvent was delivered to determine that no activity was induced by the solvent, therefore, signalling that any subsequent activity produced was a direct result of the test chemical.

An internal standard of 5% dimethyl trisulfide was also randomly applied throughout the course of screening, to eliminate the possibility of de-sensitisation of the preparation with time.

#### Taste Recordings

Non-volatile compounds were applied to gustatory chemoreceptors located on the maxillary and gustatory palps of the carabid. The test chemical was incorporated into an electrolyte in the recording electrode before being positioned over several sensillae. Any subsequent activity was stored onto computer through a specialised "delayed trigger" IADC interface box. Recordings from these sensillae produced coded responses comprising individual compound APs.

#### Feeding Trials

#### Maintenance of test animals

Carabid beetles were maintained in a controlled environment at 15°C, with a dark to light ratio of 16 hours dark to 8 hours light. Prior to feeding trials, the beetles were fed on a single blowfly maggot before being starved for a period of 5 days.

Slugs were also maintained in a controlled environment 15°C, 16 hour dark : 8 hour light ratio. Before testing the slugs were fed *ad lib* on potato and then starved for 24 hours.

#### Filter paper feeding trials

Pre-starved carabid beetles were placed in uncovered glass arenas (20cm diameter) containing two pieces of 2.5cm diameter filter paper, previously coated in 50% maggot serum. One of these paper discs was then dipped in 0.1mg/ml test chemical while the other remained untreated serving as the control. Before being placed into the arena, the filter paper was left for a period of 20 minutes to allow the solvent (n-hexane) to evaporate, each test had 10 replicates. The discs were then placed at opposite ends of the dish and moistened with distilled water. After a period of 24 hours the papers were removed and the area consumed calculated using image analysis software.

#### Slug feeding bioassays

Methiocarb-free slug pellets were placed in numbered positions on a glass plate, oven dried at 50°C and weighed. Six pre-weighed pellets were then placed in each of fifteen 9cm plastic petri dishes on two filter papers (Whatman No. 1). Each pellet was dosed with 1µL hexane solvent, thus serving as the control. The petri dishes were placed in the control environment room and the filter papers moistened with distilled water. One slug was placed in each dish and a piece of netting attached over the top to contain the slug but prevent build up of vapour from the volatile test material. After 24 hours the slugs were removed and the pellets replaced on the glass plate and re-dried. The dry weight of the pellet consumed by the slug during the test was then calculated by difference.

#### Results

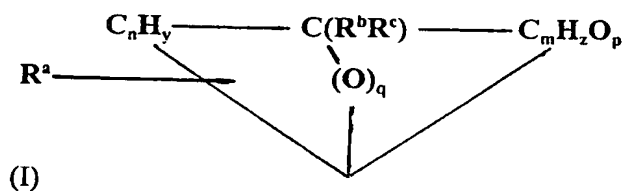
The following test compounds induced activity when screened on ten different preparations - camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one), borneol (*endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol), octan-1-ol, eucalyptol (1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane),  $\beta$ -myrcene (7-methyl-3-methylene-octa-1,6- diene), sulcatol (6-methyl-5-hepten-2-ol), sulcatone (6-methyl-5-hepten-2-one), eugenol (4-allyl-2-methoxyphenol), limonene (4-isopropyl-1-methyl-1-cyclo-hexene), *DEET* (N,N-diethyl-m-toluidine), *DMP* (dimethylphthalate),  $\alpha$ -pinene (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene), D-3-carene (3,7,7-trimethylbicyclo[4.1.0]hept-3-ene) and azadirachtin.

In the filter paper feeding trials the following compounds were tested for deterrent activity, and as such were identified as particularly useful deterrents for the present invention - borneol (*endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol), camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one), sulcatol (6-methyl-5-hepten-2-ol), sulcatone (6-methyl-5-hepten-2-one), and D-3-carene (3,7,7-trimethylbicyclo[4.1.0]hept-3-ene).

Borneol (*endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol), octan-1-ol, sulcatol (6-methyl-5-hepten-2-ol) and sulcatone (6-methyl-5-hepten-2-one) were also further tested in the slug feeding bioassays. None of these compounds substantially affected the slug feeding behaviour, as illustrated in Figures 2 and 3. In particular, sulcatol was tested at concentrations of 0.01, 0.1 and 1.0mg/ml and no detrimental effects on the slug feeding behaviour were seen.

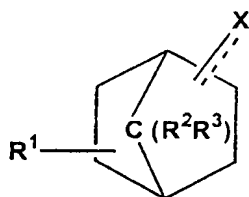
**Claims**

1. A molluscicidal composition comprising at least one molluscicide for target molluscs, and at least one deterrent for non-target invertebrates, wherein said deterrent is incorporated in the composition so as to have substantially no effect on target molluscs feeding on the composition and to substantially preclude feeding on the composition by the non-target organisms.
2. A molluscicidal composition according to claim 1, wherein said molluscicide is methiocarb.
3. A molluscicidal composition according to claim 1 or 2, wherein said deterrent comprises a bicyclic compound.
4. A molluscicidal composition according to claim 3, wherein said bicyclic compound is of the following general formula (I).

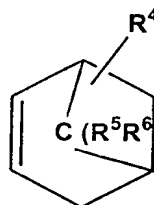


where n is 2 to 4, y is 2n or 2n-2, m is 0 to 3, z is 2m if p is 0 or 1, or z is m if p is 1, and q is 0 or 1; R<sup>a</sup>, R<sup>b</sup> and R<sup>c</sup> each independently represent hydrogen or C<sub>1-4</sub> alkyl. The oxygen in the C<sub>m</sub>H<sub>z</sub>O<sub>p</sub> group may be in a carbonyl group or a hydroxyl group, with appropriate values for m and z..

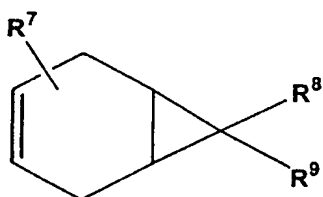
5. A molluscicidal composition according to claim 3, wherein said bicyclic compound is of the formula (II), (III), (IV) or (V)



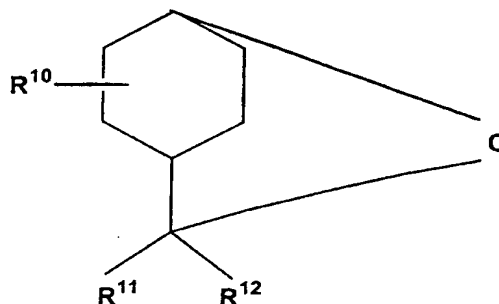
(II)



(III)



(IV)

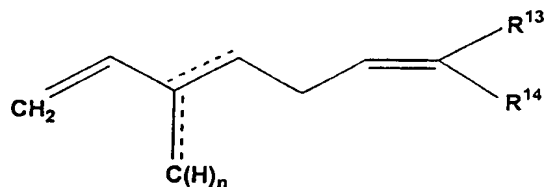


(V)

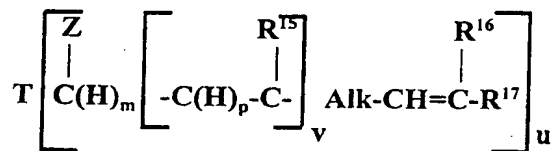
where  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$  and  $R^{12}$  each independently represent hydrogen or  $C_{1-4}$  alkyl, X represents oxygen or hydroxy and ---- represents a bond in the case where X represents oxygen.

6. A molluscicidal composition according to claim 3, wherein said bicyclic compound comprises camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one), borneol (*endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol), eucalyptol (1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane),  $\alpha$ -pinene (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene), or D-3-carene (3,7,7-trimethylbicyclo[4.1.0]hept-3-ene).

7. A molluscicidal composition according to claim 1 or 2, wherein said deterrent comprises a monohydric or polyhydric C<sub>6-10</sub> alcohol or a compound of formula (VI) or (VII)



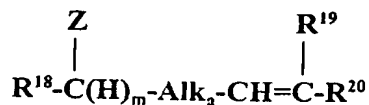
(VI)



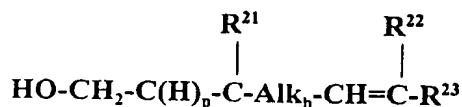
(VII)

where R<sup>13</sup>, R<sup>14</sup>, R<sup>15</sup>, R<sup>16</sup>, and R<sup>17</sup>, each independently represent C<sub>1-3</sub> alkyl, T is hydrogen or an aliphatic hydrocarbon group, Alk is a C<sub>1-3</sub> alkylene chain, Z is oxygen or hydroxy, n is 2 or 3, m is 0 or 1, v is 1 when T is hydrogen or 0 in all other cases, u is 1 or 2, p is 1 or 2 and ----- represents the optional presence of a bond.

8. A molluscicidal composition according to claim 7, wherein said deterrent is of formulae (VIII) or (IX)



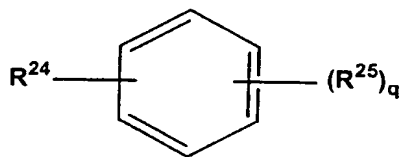
(VIII)



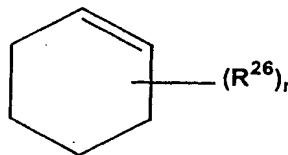
(IX)

where R<sup>18</sup>, R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup>, R<sup>22</sup>, and R<sup>23</sup> each independently represent C<sub>1-3</sub> alkyl, Alk<sub>a</sub> and Alk<sub>b</sub> independently represent a C<sub>1-3</sub> alkylene chain, Z is oxygen or hydroxy, m is 0 or 1, and p is 1 or 2.

9. A molluscicidal composition according to claim 7, wherein said deterrent comprises one or more of 2-ethylhexane-1,3-diol, citronellol (3,7-dimethyl-6-octen-1-ol), octan-1-ol,  $\beta$ -myrcene (7-methyl-3-methylene-octa-1,6-diene), nerol (*cis*-3,7-dimethyl-octa-2,6-dien-1-ol),  $\beta$ -ocimene (3,7-dimethyl-octa-1,3,6-triene), sulcatol (6-methyl-5-hepten-2-ol), sulcatone (6-methyl-5-hepten-2-one) and lycopene or a material containing lycopene..
10. A molluscicidal composition according to claim 1 or 2, wherein said deterrent comprises a substituted 6-membered carbocyclic ring, where the ring is either benzene or cyclohexene, and where the substituents are one or more of  $C_{1-4}$  alkyl,  $C_{2-4}$  alkenyl,  $C_{1-4}$  alkoxy, hydroxy,  $CO_2C_{1-4}$  alkyl,  $CON(C_{1-4} \text{ alkyl})_2$  and  $C_{1-4}$  alkylene $CON(C_{1-4} \text{ alkyl})_2$ .
11. A molluscicidal composition according to claim 10, wherein said deterrent is of formulae (X) or (XI)



(X)



(XI)

where  $R^{24}$  represents hydrogen,  $C_{1-4}$  alkyl or  $C_{2-4}$  alkenyl,  $R^{25}$  represents  $C_{1-4}$  alkyl,  $C_{1-4}$  alkoxy, hydroxy,  $CO_2C_{1-4}$  alkyl,  $CON(C_{1-4} \text{ alkyl})_2$  or  $C_{1-4}$  alkylene $CON(C_{1-4} \text{ alkyl})_2$ ,  $R^{26}$  represents  $C_{1-4}$  alkyl or  $C_{2-4}$  alkenyl,  $q$  is 1 or 2, and  $r$  is 1 or 2.

12. A molluscicidal composition according to claim 10, wherein said deterrent comprises one or more of eugenol (4-allyl-2-methoxyphenol), limonene (4-isopropyl-1-methyl-cyclohex-1-ene), *DEET* (*N,N*-diethyl-*m*-toluidine), *DEPA* (*N,N*-diethyl-phenyl-acetamide), *DMP* (dimethylphthalate) and thymol (5-methyl-2-isopropylphenol).

13. A molluscicidal composition according to claim 1 or 2, wherein said deterrent comprises a non-volatile compound.
14. A molluscicidal composition according to claim 13, wherein said non-volatile compound comprises a tetranortriterpenoid.
15. A molluscicidal composition according to any preceding claim, which includes bait material for target molluscs.
16. A molluscicidal composition according to any preceding claim, which includes food material for target molluscs.
17. A molluscicidal composition according to any preceding claim, which includes at least one inert carrier.
18. A molluscicidal composition according to any preceding claim, which is in the form of a pellet.
19. Use of a molluscicidal composition according to any preceding claim for destroying molluscs.
20. A method for destroying molluscs, which comprises providing said molluscs with a molluscicidal composition according to claim 1 to 18, wherein said mollusc is allowed to ingest said molluscicidal composition.
21. A method according to claim 20, wherein an environment is provided with said molluscicidal composition.

22. A process of preparing a molluscicidal composition which comprises mixing at least one molluscicide for target molluscs, and at least one deterrent for non-target invertebrates, said molluscicide and said deterrent being as defined in any of claims 1 to 14.
23. A process according to claim 22, in which said molluscicidal composition is mixed with at least one inert carrier.
24. A kit for use in destroying molluscs which comprises in combination at least one molluscicide for target molluscs; and at least one deterrent for non-target invertebrates, said molluscicide and said deterrent being as defined in any of claims 1 to 14.

FIGURE 1

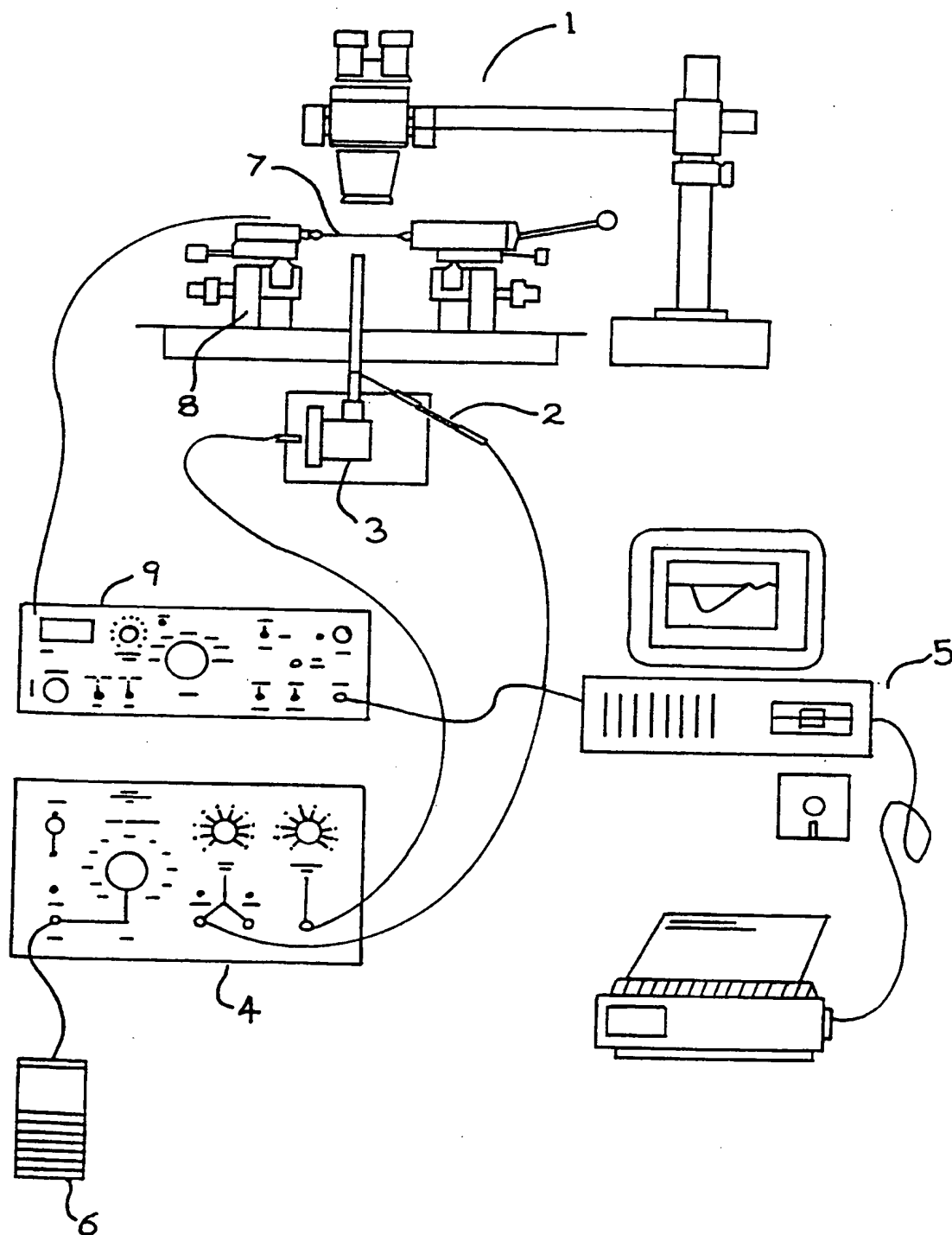


FIGURE 2

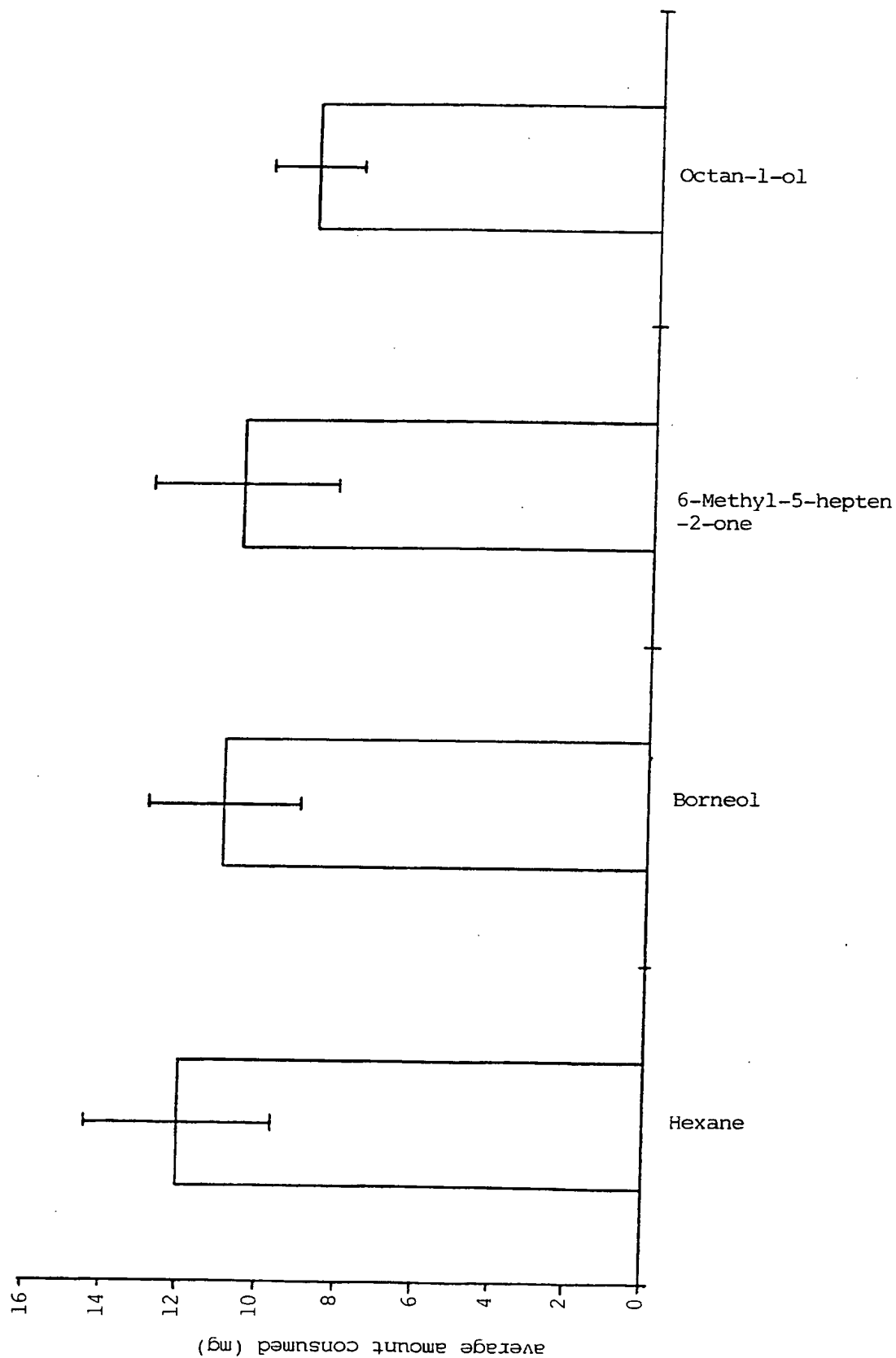
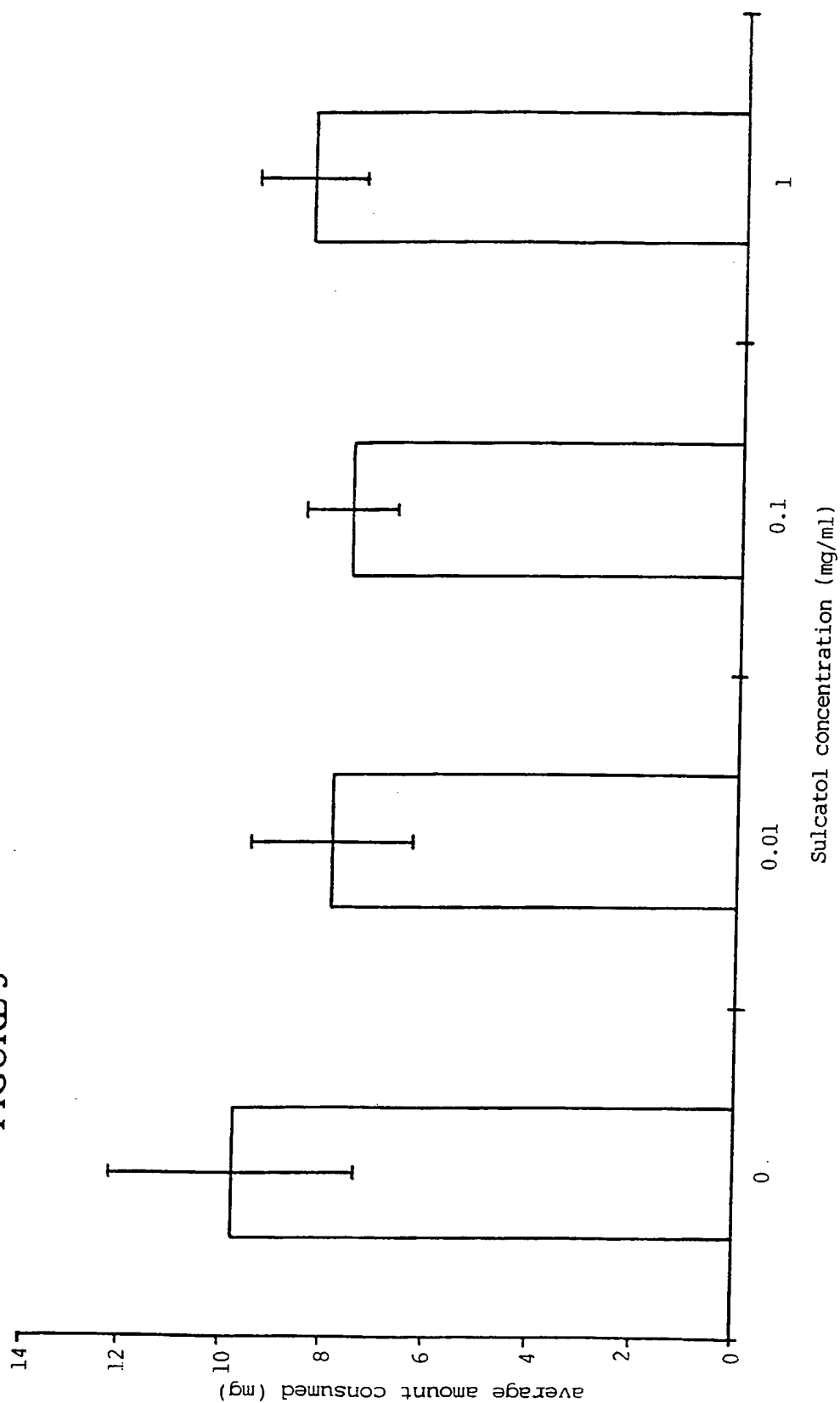


FIGURE 3



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02394

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N47/22 A01N47/24 A01N25/00 //(A01N47/22,65:00,61:00,  
49:00,43:90,37:18,37:10,35:06,35:02,31:08,31:06,35:02,31:08,  
31:06,31:02,27:00,25:00),(A01N47/24,65:00,61:00,49:00,43:90,

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 41 11 389 A (BAYER AG) 15 October 1992 (1992-10-15) the whole document	1, 2, 13, 15-24
Y		1, 3-12, 14
Y	R.WEGLER: "Chemie der Pflanzenschutz- und Schädlingsbekämpfungsmittel, Band 1" 1970, SPRINGER, BERLIN, DE XP002121255 K.H.BÜCHEL: "Insekten-Repellents", pages 487 - 496	1, 3-12, 14
Y	DE 40 12 224 A (HOLTMANN HEINRICH DR) 17 October 1991 (1991-10-17) page 2, line 3 - line 5 page 2, line 29 - line 59 --- -/--	1, 3-12, 14

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

2 November 1999

Date of mailing of the international search report

22/11/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Lamers, W

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02394

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 37:18, 37:10, 35:06, 35:02, 31:08, 31:06, 31:02, 27:00, 25:00)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DATABASE WPI Section Ch, Week 199344 Derwent Publications Ltd., London, GB; Class C03, AN 1993-348296 XP002121258 &amp; JP 05 255007 A (TUFTY GMBH), 5 October 1993 (1993-10-05) abstract</p>	1, 3-12, 14
P, X	<p>WO 98 51150 A (BOWEN IVOR ;SANGOSSE UK S A DE (GB)) 19 November 1998 (1998-11-19) page 1, paragraph 1 page 3, paragraph 4</p> <p style="text-align: center;">--- -/-- ---</p>	1, 2, 11, 13, 15-24

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

2 November 1999

Date of mailing of the international search report

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Lamers, W

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02394

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 198304 Derwent Publications Ltd., London, GB; Class C03, AN 1983-08680K XP002121259 &amp; JP 57 203003 A (HOKKO CHEM IND CO LTD), 13 December 1982 (1982-12-13) abstract</p>	1-24
A	<p>--- DATABASE WPI Section Ch, Week 198114 Derwent Publications Ltd., London, GB; Class A97, AN 1981-24453D XP002121260 &amp; JP 56 015203 A (EARTH SEIYAKU KK), 14 February 1981 (1981-02-14) abstract</p>	1-24
A	<p>--- DATABASE CABA 'Online! L.SAMSOE-PETERSEN ET AL.: "Interpretation of laboratory measured effects of slug pellets on soil dwelling invertebrates" retrieved from STN-INTERNATIONAL, accession no. 93:143105 CABA Database accession no. 931182382 XP002121256 abstract &amp; ASPECTS OF APPLIED BIOLOGY, no. 31, 1992, pages 87-96,</p>	1-24
A	<p>--- DATABASE CROPU 'Online! W.BUECHS ET AL.: "Studies on the Effect of Molluscicides on Some Carabid Beetles (Coleoptera: Carabidae) by Application in Different Laboratory and Semi-Field Tests" retrieved from STN-INTERNATIONAL, accession no. 91-83355 CROPU XP002121257 abstract &amp; Z.ANGEW.ZOOL., vol. 77, no. 3-4, 1991, pages 479-500,</p>	1-24

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/02394

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 4111389	A	15-10-1992	NONE	
DE 4012224	A	17-10-1991	NONE	
JP 5255007	A	05-10-1993	NONE	
WO 9851150	A	19-11-1998	AU 7438298 A	08-12-1998
JP 57203003	A	13-12-1982	NONE	
JP 56015203	A	14-02-1981	JP 1476800 C	27-01-1989
			JP 63020802 B	30-04-1988